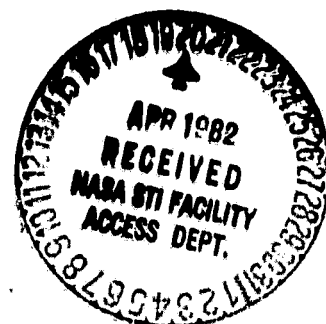


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# Optical Conductivity of $\alpha$ -Mn

K.J. Scoles and R.W. Christy

Department of Physics and Astronomy, Dartmouth College,

Hanover, NH 03755

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The optical constants were measured at room temperature in the photon-energy range 0.6 - 6.5 eV on evaporated thin films. Evaporation conditions were chosen that gave the  $\alpha$ -Mn crystal structure with reasonably large grains. The optical conductivity was separated into intraband and interband contributions by fitting to the Drude formula at low energies. The results are anomalous in comparison to other 3d transition metals: The free-electron lifetime is exceptionally short (in agreement with the large dc resistivity of Mn), and the interband transitions seem unusually weak at the lower energies. We discuss possible explanations related to the complicated crystal structure of  $\alpha$ -Mn.

Previous optical studies<sup>1-3</sup> of d-band metals from 0.5 to 6.5 eV suggest that manganese is somewhat anomalous among these elements. Most show regularities, some of which have been interpreted in terms of theoretical calculations of the optical conductivity,  $\hat{\sigma} = \sigma_1 + i\sigma_2$ . In particular, the real part of the conductivity  $\sigma_1$  for each of the 3d elements shows a peak in the vicinity of 6 eV with a height of  $3-5 \times 10^{15} \text{ s}^{-1}$  in cgs units, and another, usually higher, peak around 2.5 eV. On the basis of detailed calculations including matrix elements throughout the Brillouin zone,<sup>4</sup> the peak near 6 eV has been assigned mainly to transitions from band 1  $\rightarrow$  6 in vanadium,<sup>2,3</sup> chromium,<sup>2,3</sup> and nickel,<sup>1,2</sup> as well as copper;<sup>1</sup> the peak near 2.5 eV was due mainly to band 3  $\rightarrow$  5 transitions in V, Cr, and Ni (but 5  $\rightarrow$  6 in Cu, where the Fermi energy is now higher than band 5). Manganese shows a peak near 6 eV; but at lower photon energies the conductivity is much flatter. Figure 1 shows our present data for Mn, in comparison to V, Cr, and Fe— its neighbors in the third row of the periodic table.

The dc conductivity of Mn is also peculiar.<sup>5</sup> Its resistivity is extremely large, 150 - 500  $\mu\Omega\text{cm}$  at room temperature,<sup>6</sup> within the range of metallic glasses. (In terms of resistivity, cgs  $10^{-15} \text{ s} = 900 \mu\Omega\text{cm}$ .) It is very sensitive to impurities and heat treatment, but in the best cases it falls to a residual value of the order of 10  $\mu\Omega\text{cm}$  at liquid-helium temperatures. Measurements on evaporated films<sup>7,8</sup> are consistent with the bulk results.

The stable crystal structure of manganese is also unusual: among the other transition metals, it is the only one with a complex structure (i.e., other than bcc, fcc, or hcp). The structure of  $\alpha$ -Mn has a bcc unit cell containing 58 atoms.<sup>9</sup> Its neighbors V, Cr, and Fe, have the simple bcc structure.

Our purpose here was to make a more detailed study of the optical properties of  $\alpha$ -Mn films. Manganese of 99.95% purity (Alpha Inorganics) was treated with hydrochloric acid to remove oxide, and then electron-beam evaporated in high vacuum ( $5 \times 10^{-7}$  Torr or  $7 \times 10^{-5}$  Pa) onto fused-silica substrates at fast rates (about  $100 \text{ \AA/s}$ ). In order to obtain large-grained films of pure  $\alpha$ -Mn, the substrate was backed by tantalum foil heated to around  $700^\circ\text{C}$  during deposition. Subsequent x-ray diffractometer measurements of the samples showed only the (033) line of  $\alpha$ -Mn. The line position gave a lattice constant of  $8.858 \text{ \AA}$ , about 0.6% less than the ASTM value, perhaps because of a tensile strain in the plane of the film. The line width indicated according to the Scherrer equation a grain size greater than  $400 \text{ \AA}$  (the limit of resolution determined by the diffractometer slit width) for thick films, and thickness-limited for thin films. Evaporation onto room-temperature substrates yielded a rather fine-grained mixture of  $\alpha$ -Mn,  $\beta$ -Mn, and Mn-sublimate structures instead.

The method of obtaining the optical constants and film thickness from reflectance and transmittance measurements has been described previously.<sup>2,3</sup> These measurements were made on films in the thickness range  $300 - 450 \text{ \AA}$ . The optical conductivity of  $\alpha$ -Mn is shown again in Fig. 2, along with its imaginary part  $\sigma_2$ . (The real susceptibility is  $\chi_1 = -\sigma_2/\omega$ .) Because of the

relatively large grain size, no grain-boundary effects<sup>10</sup> are expected in these films. The conductivity of the  $\alpha$ -Mn films was not radically different from that of our films evaporated onto room-temperature substrates, which agreed approximately with the earlier results.<sup>2</sup> All the optical measurements were made after the samples were removed from the vacuum system, but oxidation was retarded by back-filling the vacuum system with nitrogen before opening and by flowing nitrogen through the spectrophotometer.<sup>2,11</sup>

The rather flat behavior of the optical conductivity at low photon energy, together with the very large dc resistivity, is suggestive of the Drude free-electron result with a very short electron lifetime  $\tau$ . In fact, the optical  $\sigma_1$  seems to be tending to about  $4 \times 10^{15} \text{ s}^{-1}$  at  $\omega = 0$ , i.e., to a resistivity of about  $225 \text{ } \mu\Omega\text{cm}$  in approximate agreement with measured dc values. Therefore we have used the Drude formula

$$\frac{\sigma_0}{1-i\omega\tau} = \frac{\sigma_0}{1+(\omega\tau)^2} + i \frac{\sigma_0\omega\tau}{1+(\omega\tau)^2} = \sigma_1 + i\sigma_2$$

in order to estimate the free-electron contribution to the measured conductivity of  $\alpha$ -Mn. The dashed curves in Fig. 2 show the result of subtracting the Drude values from the solid curves if we choose  $\sigma_0 = 4 \times 10^{15} \text{ s}^{-1}$  and  $\tau = 0.33 \times 10^{-15} \text{ s}$ , and they represent interband contributions to the conductivity which will be discussed below. The  $\sigma_0$  value was chosen on the basis of dc measurements, but the  $\tau$  value is more problematical. It is difficult to establish values of the Drude lifetime from infrared optical measurements on transition metals,<sup>2,3</sup> and in

particular no values are known for Mn. For purposes of our analysis, we chose a value that makes the interband contributions of  $\sigma_1$  and  $\sigma_2$  tend properly toward zero at  $\omega = 0$ . In fact, the value of  $\tau$  is limited by the following considerations based on the free-electron theory: Since

$$\sigma_0 = (ne^2/m^*)\tau,$$

an assumption about  $\tau$  is equivalent to an assumption about the effective electron density  $n$  or the effective mass  $m^*$ ; the above value would correspond to 0.6 free electrons per Mn atom with the free-electron mass. This number gives a free-electron Fermi velocity,

$$v_F = \hbar(3\pi^2 n)^{1/3}/m^*,$$

of  $1.3 \times 10^9$  cm/s and a mean free path

$$\lambda = v_F \tau = (\hbar/e^2)\sigma_0(3\pi^2/n^2)^{1/3}$$

of  $4.4 \text{ \AA}$ , just greater than the interatomic distance of about  $2.3 \text{ \AA}$ . The mean free path could not be much shorter, and therefore the effective electron number cannot be more than about 1 per atom; if we also assume that  $m^*/m \geq 1$ , then  $\tau$  cannot be much less than the chosen value. On the other hand, it cannot be much greater either: As noted above, in the most perfect samples the dc resistivity falls by more than an order of magnitude at low temperature; since the factor  $n/m^*$  is not likely to have a strong temperature dependence, we attribute the large room-temperature resistivity to a small value of  $\tau$ . Thus we believe that this rough estimate is probably good to within

about a factor of 2, giving an error bar for the free-electron  $\sigma_1$  of about  $\pm 1 \times 10^{15} \text{ s}^{-1}$  at  $\hbar\omega = 2 \text{ eV}$ . Qualitatively, the large optical free-electron  $\sigma_1$  for Mn, in comparison with the other transition metals, is related to its much smaller  $\sigma_0$  value (since  $\sigma_0$  is proportional to  $\tau$  but  $\tau^2$  appears in the Drude denominator).

Recognizing the uncertainty in our separation of the optical conductivity into free-electron and interband contributions, we can still make some observations about the interband  $\sigma_1$  of Mn in comparison to the other 3d metals. It seems certain that there is a peak near 6 eV, whose magnitude is comparable with those of the other metals. A lower energy peak is also discernable near 2.5 eV, but its magnitude is definitely much smaller than in the other metals.

It is tempting to try to link the electrical and optical peculiarities of Mn to its uniquely complicated crystal structure. No theoretical energy-band calculations have been done for this structure, but a calculation for Mn with the fcc structure<sup>12</sup> does not suggest that there would be any abnormalities for this particular element. We may thus speculate on the effects that a large (29-atom) unit cell might have on an otherwise-normal band picture. For each d-electron branch in the primitive bcc or fcc Brillouin zone, there would be 29 branches in the  $\alpha$ -Mn zone. Actually, many of these would be degenerate, since there are just four different types of atom sites in the structure,<sup>9</sup> but still one would expect a significant proliferation of branches at a given  $\mathbf{k}$  vector and fragmentation of the Fermi surface. The

effect on scattering of the free electrons might be to increase the number of possibilities for umklapp scattering, and thus give the very large temperature dependence that is observed in the dc resistivity at low temperature. The effect on the inter-band conductivity would seem to be to increase the number of d-to-d-band transitions across the Fermi surface that are available at any given  $k$ , and thus to spread out the low-energy conductivity peaks. The observation that the magnitude of the low-energy absorption is smaller than expected must mean a reduction in oscillator strengths (matrix element). Possibly the loss of symmetry within the cell reduces the amount of mixing of the d states with s-p states, so that the forbidden character of atomic d-to-d transitions is more important (for example in the  $3 \rightarrow 5$  transitions). The  $1 \rightarrow 6$  transitions responsible for the 6-eV peak are basically of d-to-p character, and would be less affected.

Since  $\alpha$ -Mn is antiferromagnetic below the Néel temperature of about 95 K, the effects of magnetic scattering of the free electrons are important and the large room-temperature resistivity is attributed to spin-disorder scattering.<sup>13</sup> In this connection a comparison with Cr is interesting, since Cr is antiferromagnetic with a Néel temperature of 311 K but has the bcc structure. The dc resistivity of Cr shows features associated with the magnetic phase transition in an interval of about 10 degrees around the transition temperature,<sup>14</sup> but otherwise the resistivity is not unusual.<sup>15</sup> The maximum-minimum feature in the resistivity of Mn at its Néel point is quite similar to that in Cr, the difference being the large saturation resistivity attained by Mn at this temperature. A possible mechanism might



be the facilitation of umklapp in spin-wave scattering for  $\alpha$ -Mn due to its complicated crystal structure. Another indication of the role of the complex structure of  $\alpha$ -Mn may be the lower resistivity observed in the simpler  $\beta$ - and (fcc)  $\gamma$ -Mn structures.<sup>16</sup>

We conclude that the optical absorption of  $\alpha$ -Mn is anomalous in part because the intraband contribution has an exceptionally short electron lifetime (with a mean free path close to the minimum possible), which is consistent with measured dc resistivity. Secondly, the interband part shows a somewhat reduced oscillator strength for the lower-energy transitions, compared to what might be expected. We suggest that both these results may be related to the complex  $\alpha$ -Mn crystal structure.<sup>17</sup>

We thank Professor W.E. Lawrence for helpful discussions, and NASA for the support of this work.

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## FIGURE CAPTIONS

Fig. 1 The real part of optical conductivity of  $\alpha$ -Mn (present work), in comparison with V and Cr (Ref. 3) and Fe (Ref. 2). The Fe curve is displaced downward by 4 units, and the Cr and V curves are displaced upward by 4 and 8 units, respectively.

Fig. 2 The real and imaginary parts of optical conductivity of  $\alpha$ -Mn (solid curve), and after subtraction of an assumed Drude contribution with  $\sigma_0 = 4 \times 10^{15} \text{ s}^{-1}$  and  $\tau = 0.33 \times 10^{-15} \text{ s}$  (dashed curve).

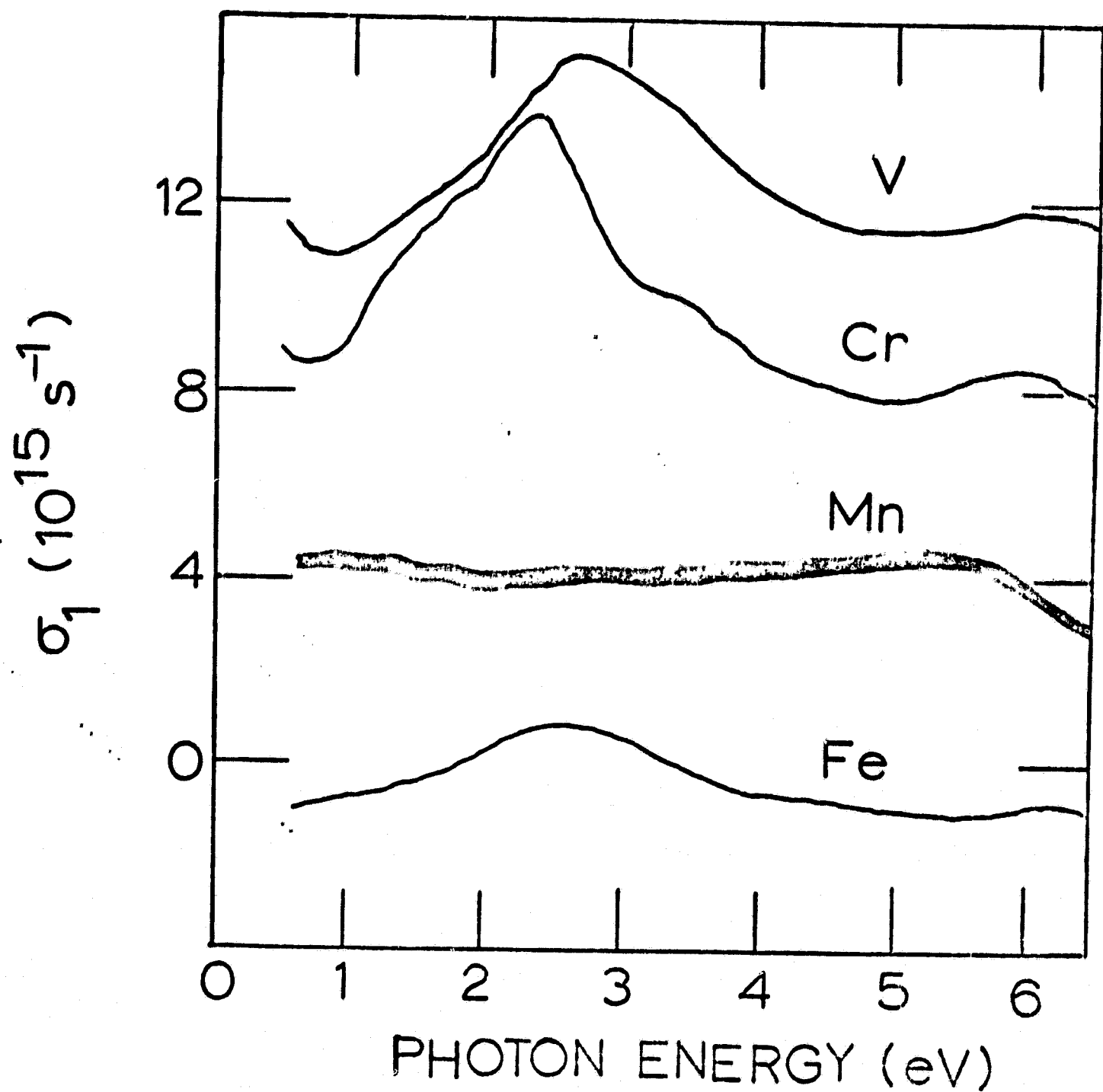


Fig. 1

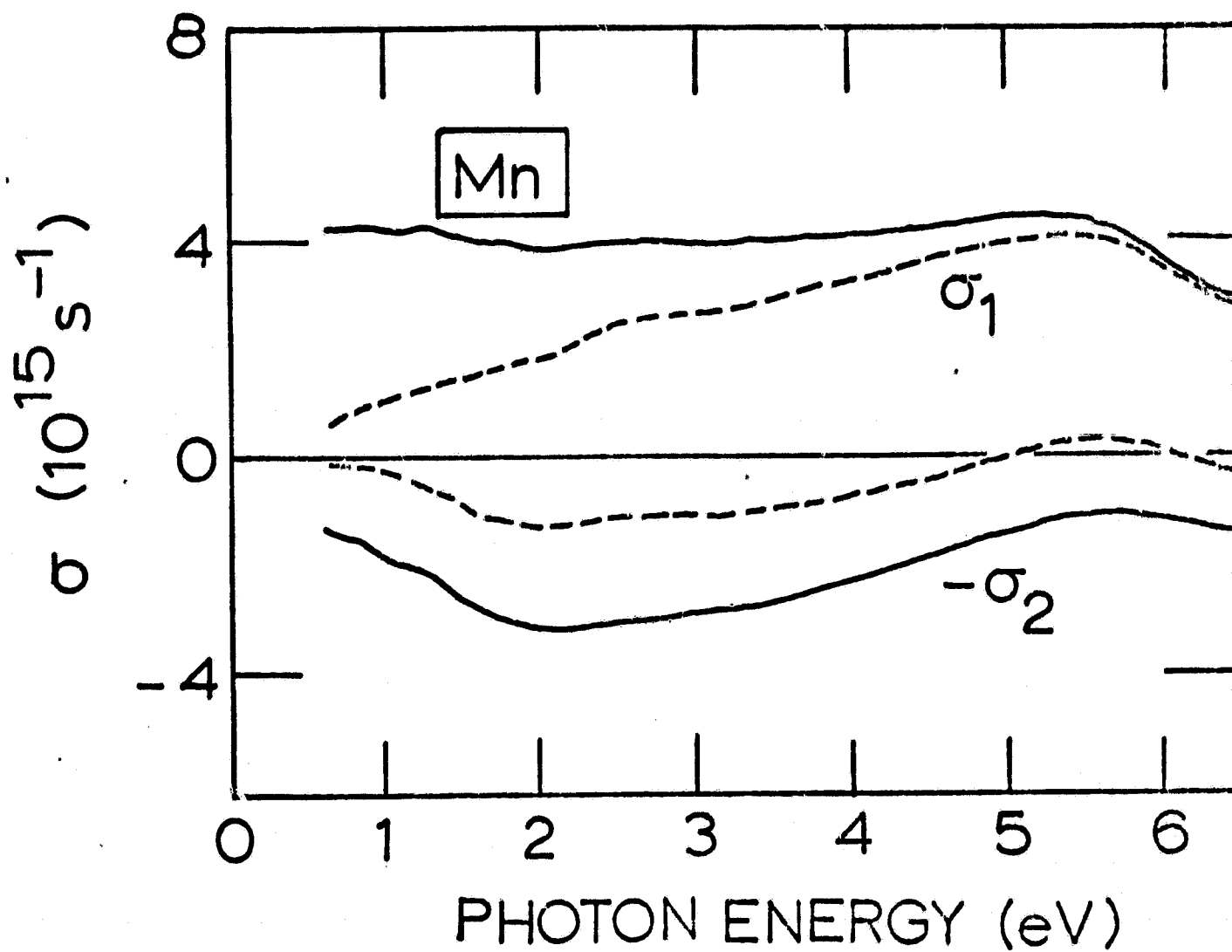


Fig.2